NUCLEAR SCIENCE AND TECHNIQUES **25**, 030202 (2014)

PIXE analysis of proto-porcelain excavated from Tingziqiao kiln site of Deqing (China)*

ZHANG Bin (张斌),[1,†] CHENG Huan-Sheng (承焕生),[1] and ZHENG Jian-Ming (郑建明)[2]

[1] *Institute of Modern Physics, Fudan University, Shanghai 200433, China*
[2] *Institute of Cultural Relics and Archaeology of Zhejiang Province , Hangzhou 310014, China*
(Received September 13, 2013; accepted in revised form December 17, 2013; published online June 20, 2014)

Particle induced X-ray Emission (PIXE) was used to analyze the proto-porcelain excavated from Tingziqiao kiln site of Warring States (475–221 BC) in Deqing County of Zhejiang Province, China. It was found that the porcelain body and glaze differ from each other in recipes. The porcelain clay of high silicon and low aluminum might be used to make the body of proto-porcelain. Lime and plant or wood ashes might be added into the glaze of the proto-porcelain. Cluster analysis was done to reveal the compositional relationship between the proto-porcelain samples.

Keywords: PIXE, Proto-porcelain, Cluster analysis

DOI: 10.13538/j.1001-8042/nst.25.030202

I. INTRODUCTION

Proto-porcelains are porcelain products of the original stage. From October 2007 to March 2008, many proto-porcelains were excavated from Tingziqiao kiln site of Warring States (475–221 BC) in Deqing County of Zhejiang Province, China. The archaeological information of them includes the source of porcelain, the porcelain-making technology, etc. To obtain this information, it is important to determine chemical compositions of the proto-porcelains. Particle induced X-ray Emission (PIXE) [1–3] is an efficient technique to analyze the archaeological samples. It allows a quick multi-element determination of element concentrations with the ppm sensitivity.

At Fudan University, the PIXE technique has been used systematically to study ancient Chinese pottery and porcelain [4–6]. Recently, we did a PIXE study on ancient Chinese proto-porcelains. In this paper, we report the results of the proto-porcelains unearthed from Tingziqiao kiln site by using PIXE. Among many chemical compositions, we try to find the elemental features that would be characteristic or specific for the proto-porcelains. We also hope to find the compositional relationship between the proto-porcelain samples and attempt to explore the technology of making proto-porcelain.

II. EXPERIMENTAL

Eighteen proto-porcelain samples excavated from Tingziqiao kiln site, coded as DTT303⑤: 1–7 and DTT303⑤: 9–19, were provided by archaeologists at Institute of Cultural Relics and Archaeology of Zhejiang Province. They were of jar shapes, with grey body and straw-yellow glaze.

The PIXE analysis was performed on the NEC 9SDH-2 3 MV pelletron tandem accelerator of Fudan University. External proton beams of 3 MeV were used to determine chemical compositions of the proto-porcelain samples, which were placed at 10 mm outside the beam exit window (7.5 μm Kapton film). As a result of energy loss in the Kapton film and air, the protons reaching the samples was 2.8 MeV in energy. The beam spot diameter on the sample was 1 mm and the beam current was 0.05 nA, so as to keep the dead time at less than 3%. A Si(Li) detector (SGX Sensortech (MA) Ltd, with an energy resolution of 150 eV FWHM at 5.9 keV) placed perpendicular to the beam direction, was used to detect the X-rays emitted from the sample. X-rays traveled through 15 mm of fluid helium gas before reaching the detector. The PIXE spectra were collected with conventional electronics and a multi-channel analyzer. The net counts of characteristic X-ray peaks were obtained after background fitting and subtraction using the GUPIX-96 code [7]. A reference sample GSD-6, of which element contents had been analyzed by the Inductive Coupled Plasma Emission Spectrometer (ICP) method, was used to determine the PIXE parameters.

Glaze thickness of the proto-porcelain samples was not uniform. The thinnest glaze is about 0.1 mm, which is about the projection range of 2.8 MeV protons in porcelain glaze. Therefore, these locations were not suitable for analyzing the glaze chemical compositions, which would have been affected by added information from the porcelain body if the protons penetrated the glaze and went into the body. To avoid the body effect on glaze, thick glaze locations, in sizes bigger than the proton beam spot, were selected for the PIXE measurements.

III. RESULTS AND DISCUSSION

Typical PIXE spectra of the body and glaze of DTT303⑤:1 sample are shown in Fig. 1. The X-ray peaks from Na, Mg, Al, Si, P, K, Ca, Ti, Cr, Mn and Fe can be seen clearly. The contents of Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, Cr_2O_3, MnO and Fe_2O_3, in the porcelain body and glaze were obtained from the PIXE analysis, as listed in Tables 1 and 2, respectively.

Cluster analysis [8] was used to study the compositional

* Supported by the compass special plan from the bureau of cultural relics of China
† Corresponding author, binzhang@fudan.edu.cn

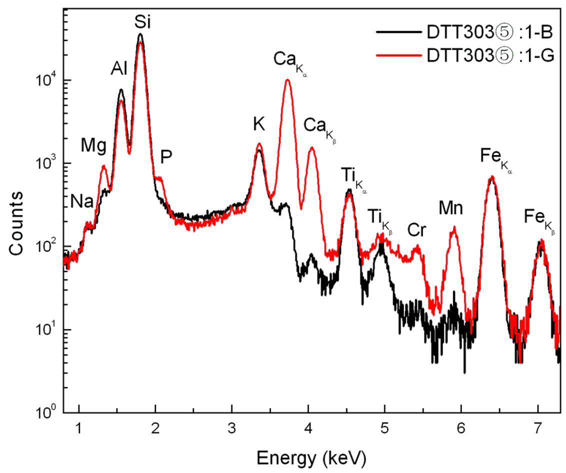

Fig. 1. (Color online) Typical PIXE spectra from DTT303⑤:1, a proto-porcelain sample excavated from Tingziqiao kiln cite. The B and G denote body and glaze of the porcelain sample, respectively.

relationship between the proto-porcelain samples. The chemical compositions in Tables 1 and 2 were chosen as variables, and the samples were clustered step by step. The results of cluster analysis only reflect the intimate or aloof relationships between samples, which are only related to the chemical compositions in body or glaze (namely the raw materials), not to the ware shape and age. The dendrogram obtained is showed in Fig. 2, where the samples are divided into Groups 1 and 2, respectively corresponding to the porcelain body and glaze. This means that the body and glaze of the proto-porcelain differ from each other in their recipes. The body samples are faster clustered together than the glaze samples, implying that the dispersity of body chemical compositions is smaller than that of the glaze.

In Table 1, the body contents of Al_2O_3 and Fe_2O_3 are 13.74%–16.94% and 2.19%–3.29%, respectively, while the SiO_2 content is 75.31%–79.89%. This feature of high silicon and low aluminum of the proto-porcelain body is similar to that of porcelain clay [9], which is abundant in southern China. This kind of porcelain clay might be used to make the body of proto-porcelain.

In Table 2, the glaze CaO content (13.56%–23.75%) is much higher than that of K_2O (1.4%–3.76%), indicating that lime might be used in making proto-porcelain. Hence, the glaze of proto-porcelain is also called Ca-rich glaze. The P_2O_5 content (0.64%–1.35%) in glaze is much higher than that in the body (0.03%–0.38%), suggesting that plant or wood ashes might also be added into the glaze during proto-porcelain production. Wu *et al.* [10] reported the major compositions of body and glaze of proto-porcelains unearthed from Fengjiashan kiln site of Warring States (475–221 BC) in Deqing County of Zhejiang Province, China. The average body contents of Al_2O_3 and SiO_2 were 15.85% and 77.34%, respectively, while the average glaze CaO content was 16.35%. These results are the same as ours.

From Fig. 2, the body samples can be divided into three sub-clusters. Samples DTT303⑤:11-B and DTT303⑤:13-B cluster together as Sub-cluster 1 because of their low Al_2O_3 contents (13.74%–14.16%) and high SiO_2 contents (79.4%–79.89%), while Samples DTT303⑤:5-B, DTT303⑤:6-B, DTT303⑤:7-B, DTT303⑤:9-B, DTT303⑤:10-B, DTT303⑤:18-B and DTT303⑤:19-B cluster together as Sub-cluster 2 because of their high Al_2O_3 contents (16.04%–16.94%) and low SiO_2 contents (75.31%–76.61%). The other body samples cluster together because their contents of Al_2O_3 (14.4%–15.66%) and SiO_2 (77.04%–78.77%) differ from those of Sub-clusters 1 and 2.

The glaze samples can be divided into three sub-clusters, too. Samples DTT303⑤:4-G, DTT303⑤:10-G and DTT303⑤:19-G, with higher CaO content (19.56%–23.75%) and lower content of SiO_2 (53.75%–57.07%), are far away from the other glaze samples. Samples DTT303⑤:2-G, DTT303⑤:3-G, DTT303⑤:5-G, DTT303⑤:7-G, DTT303⑤:11-G, DTT303⑤:12-G and DTT303⑤:13-G cluster together because their low SiO_2 (58.95%–59.9%) and high CaO (16.54%–19.47%) contents, while Samples DTT303⑤:1-G, DTT303⑤:6-G, DTT303⑤:9-G, DTT303⑤:14-G, DTT303⑤:15-G, DTT303⑤:16-G, DTT303⑤:17-G and DTT303⑤:18-G cluster together because of their high SiO_2 (60.95%–63.78%) and low CaO (13.56%–16.32%) contents.

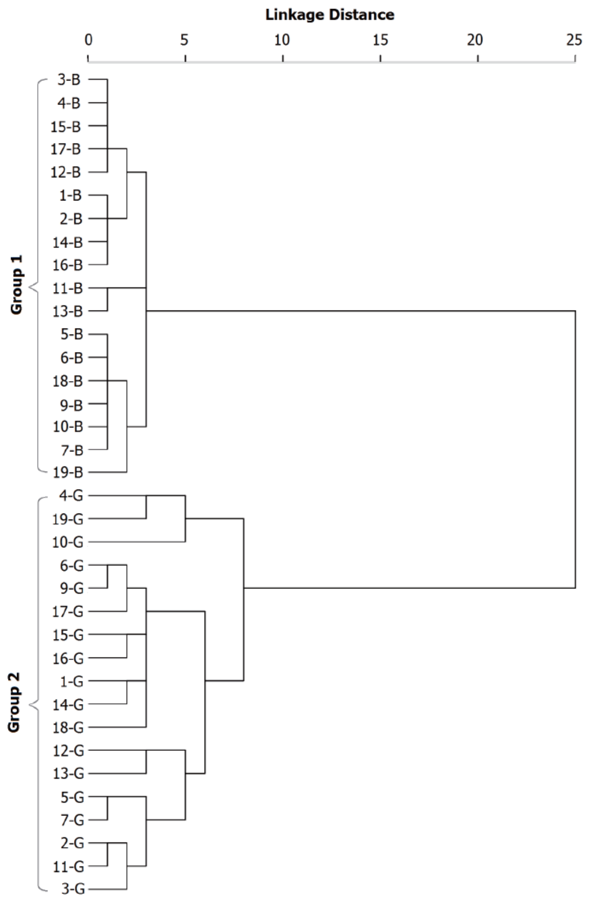

Fig. 2. Cluster analysis dendrogram of the proto-porcelain samples based on their chemical compositions.

TABLE 1. Body chemical compositions (wt%) of the DTT303⑤ proto-porcelains from Tingziqiao kiln site

No.	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3
DTT303⑤:1-B	0.41	0.62	15.42	77.43	0.27	1.84	0.41	1.15	0.01	0.02	2.42
DTT303⑤:2-B	0.45	0.57	15.24	77.54	0.15	1.90	0.40	1.22	0.01	0.03	2.49
DTT303⑤:3-B	0.41	0.60	14.90	77.88	0.11	1.95	0.39	1.10	0.02	0.03	2.61
DTT303⑤:4-B	0.39	0.58	14.83	78.08	0.11	1.90	0.41	1.16	0.02	0.02	2.50
DTT303⑤:5-B	0.62	0.62	16.19	76.61	0.33	1.59	0.35	1.02	0	0.03	2.64
DTT303⑤:6-B	0.39	0.72	16.16	76.58	0.15	1.67	0.28	1.10	0.02	0.02	2.90
DTT303⑤:7-B	0.58	0.76	16.80	76.18	0.38	1.57	0.32	1.12	0.01	0.02	2.25
DTT303⑤:9-B	0.41	0.70	16.47	75.93	0.32	1.86	0.36	1.15	0.01	0.02	2.77
DTT303⑤:10-B	0.66	0.52	16.94	75.74	0.17	1.74	0.43	1.03	0.01	0.02	2.74
DTT303⑤:11-B	0.51	0.53	14.16	79.40	0.14	1.49	0.27	1.11	0.01	0.02	2.36
DTT303⑤:12-B	0.43	0.53	14.40	78.77	0.14	1.69	0.31	1.15	0.01	0.02	2.54
DTT303⑤:13-B	0.40	0.52	13.74	79.89	0.32	1.54	0.26	1.10	0.02	0.02	2.19
DTT303⑤:14-B	0.30	0.61	15.55	77.04	0.20	1.99	0.39	1.12	0.01	0.02	2.77
DTT303⑤:15-B	0.29	0.49	14.64	78.38	0.14	1.93	0.37	1.22	0.01	0.03	2.50
DTT303⑤:16-B	0.30	0.60	15.66	77.20	0.21	1.93	0.36	1.13	0.02	0.01	2.58
DTT303⑤:17-B	0.23	0.57	14.70	77.96	0.17	1.86	0.33	1.10	0.01	0.02	3.05
DTT303⑤:18-B	0.43	0.63	16.04	76.39	0.08	2.09	0.43	1.24	0.02	0.03	2.61
DTT303⑤:19-B	0.28	0.69	16.53	75.31	0.03	2.17	0.48	1.17	0	0.05	3.29

TABLE 2. Glaze chemical compositions (wt%) of the DTT303⑤ proto-porcelains from Tingziqiao kiln site

No.	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3
DTT303⑤:1-G	0.43	2.23	12.23	61.52	1.16	1.94	16.32	0.98	0.10	0.44	2.65
DTT303⑤:2-G	0.40	2.09	11.43	59.57	1.34	1.68	18.94	1.03	0	0.53	2.99
DTT303⑤:3-G	0.31	2.01	12.53	59.50	1.34	1.71	17.87	1.10	0	0.52	3.11
DTT303⑤:4-G	0.36	2.11	11.44	57.07	1.33	1.86	19.56	1.07	0.05	0.73	4.42
DTT303⑤:5-G	0.41	2.60	13.37	59.26	1.24	2.11	16.96	0.82	0.13	0.42	2.69
DTT303⑤:6-G	0.58	2.22	12.65	60.96	0.94	2.67	13.96	1.13	0.06	0.81	4.02
DTT303⑤:7-G	0.81	3.02	13.72	59.31	1.17	1.97	16.54	0.79	0.21	0.41	2.05
DTT303⑤:9-G	0.53	2.04	13.47	60.95	0.65	2.69	13.69	1.08	0.05	0.35	4.48
DTT303⑤:10-G	0.37	2.20	11.07	53.75	1.24	1.55	23.75	1.01	0.03	0.80	4.22
DTT303⑤:11-G	0.72	2.45	11.69	58.95	1.25	2.15	18.55	0.94	0.12	0.35	2.81
DTT303⑤:12-G	0.38	1.83	9.25	59.90	0.88	1.63	18.38	1.05	0.03	0.86	5.81
DTT303⑤:13-G	0.36	1.93	9.77	59.60	1.35	2.11	19.47	1.02	0.01	0.46	3.92
DTT303⑤:14-G	0.61	2.18	13.03	61.94	0.95	1.58	14.79	1.01	0.06	0.58	3.26
DTT303⑤:15-G	0.57	2.05	12.27	63.78	0.97	2.31	14.25	1.02	0	0.27	2.50
DTT303⑤:16-G	0.45	1.79	11.65	63.45	0.72	2.14	14.42	1.01	0.09	0.41	3.85
DTT303⑤:17-G	0.42	2.14	12.40	61.48	1.29	2.25	13.56	1.04	0.03	0.48	4.90
DTT303⑤:18-G	0.81	1.75	12.61	61.76	0.64	3.76	15.36	0.96	0.05	0.21	2.09
DTT303⑤:19-G	0.36	2.66	11.80	56.00	1.04	1.40	21.45	1.00	0.07	0.84	3.38

IV. CONCLUSION

The body and glaze of the proto-porcelain differ from each other in their recipe. The porcelain clay of high silicon and low aluminum might be used to make the porcelain body. Lime and plant or wood ashes might be added into the glaze in making proto-porcelain. Cluster analysis discloses the compositional relationship between the proto-porcelain samples.

ACKNOWLEDGEMENTS

This work is supported by the compass special plan from the bureau of cultural relics of China.

[1] Cheng H S, He W Q, Tang J Y, *et al*. Nucl Instrum Meth B, 1996, **118**: 377–381.
[2] Cheng H S, Zhang Z Q, Xia H N, *et al*. Nucl Instrum Meth B, 2002, **190**: 488–491.
[3] Zhang B, Yao S D, Wang K, *et al*. J Radioanal Nucl Chem, 2006, **269**: 9–13.
[4] Zhang B, Pan B H, Zhang Z Q, *et al*. Nucl Instrum Meth B, 2004, **219–220**: 26–29.

[5] Zhang B, Cheng H S, Zhao W J, *et al*. X-Ray Spectrom, 2006, **35**: 27–32.
[6] Zhu D, Cheng H S, Lin J W, *et al*. Nucl Instrum Meth B, 2006, **249**: 633–637.
[7] Campbell J L, Hopman T L, Maxwell J A, *et al*. Nucl Instrum Meth B, 2000, **170**: 193–204.
[8] Luo H. Chinese Ancient Ceramics and Multivariate Statistical Analysis, Chinese Light Industry Publishing Company, Beijing, 1997, 9.
[9] Li J Z. J Build Mater, 2000, **3**: 7–13. (in Chinese)
[10] Wu J, Zhang M L, Wu J M, *et al*. J of Build Mater, 2011, **14**: 659–663. (in Chinese)